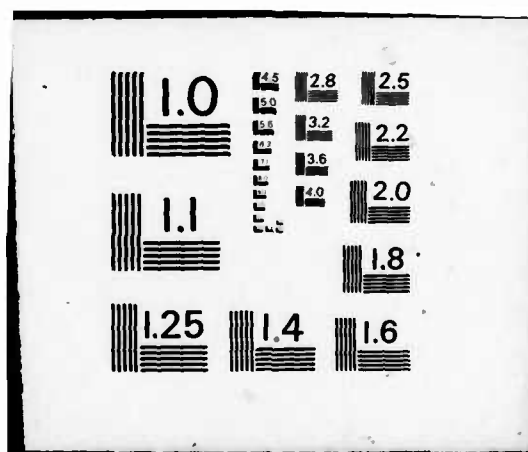ADA035313

Technical Report No. 8

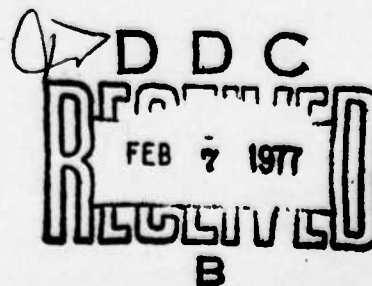DYNAMIC MECHANICAL PROPERTIES OF SOLVENT CRAZED POLYSTYRENE

by

B. A. Shah, G. Akovali* and M. Shen
Department of Chemical Engineering
University of California
Berkeley, California 94720

September 1, 1976

D D C

FEB 7 1977

RECEIVED

B

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Dynamic Mechanical Properties of Solvent Crazed Polystyrene,		5. TYPE OF REPORT & PERIOD COVERED Technical Report.,
		6. PERFORMING ORG. REPORT NUMBER TR-8
7. AUTHOR(s) B. A. Shah, G. Akovali and M. Shen		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0955
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemical Engineering University of California Berkeley, California 94720		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 11 P.
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217		12. REPORT DATE 1 Sep 76
		13. NUMBER OF PAGES 8
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release: Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Solvent Crazing, Polystyrene, Dynamic Mechanical Properties.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The dynamic mechanical properties of polystyrene crazed in various organic solvents were determined on a Rheovibron Visco-elastometer. It was found that the loss curves for polystyrene crazed in the presence of ethylene glycol, diethylene glycol and triethylene glycol were similar to the uncrazed polystyrene. However, when 1-pentanol was used as the solvent, there is a substantial decrease in the glass transition temperature of

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

polystyrene. The latter evidence is in clear agreement with the plasticization mechanism of solvent crazing. However, the former data with the glycols seem to indicate that the surface stabilization mechanism cannot be ruled out.
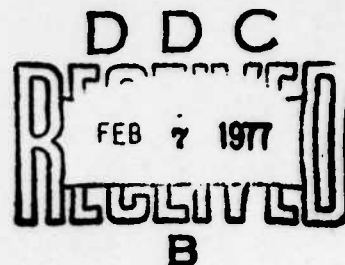
DYNAMIC MECHANICAL PROPERTIES OF SOLVENT CRAZED POLYSTYRENE

by

B. A. Shah, G. Akovali* and M. Shen
Department of Chemical Engineering
University of California
Berkeley, California 94720

Glassy polymers often exhibit drastic reduction in strength when exposed to certain organic solvents. A number of mechanisms have been proposed to account for this phenomenon of solvent crazing, which were recently reviewed by Kambour[1]. In this communication, we wish to report on the dynamic mechanical properties of solvent-crazed polystyrene in order to gain further insight into the mechanism of this process.

Polystyrene was purchased from the Polysciences, Inc. Gel permeation chromatographic measurements indicate that its number average molecular weight is 74,800. The polymer was dissolved in benzene, and films were cast from the solution by means of spin casting[2]. Rectangle strips of the sample were deformed in the presence of a number of organic solvents by a specially constructed creep instrument. After the crazes have formed, the sample was removed from the creep instrument and surface dried. It was then immediately transferred to the sample chamber of a Rheovibron DDV-IIB Viscoelastomer. In order to minimize solvent loss during measurements, the sample chamber was modified to contain the organic liquid at the bottom of the chamber (without

---

* Present Address: Department of Chemistry, Middle East Technical University, Ankara, Turkey

touching the sample). Because of the extensive crazing, samples were very fragile and great care must be taken during the experimentation. Only one frequency (3.5 Hz) was found to be usable without fracturing the sample. Data were taken to the maximum temperature before rupture.

Table 1 shows the relevant characteristics of the solvents[3] used in this study. Polystyrene was crazed by deforming to just below the critical strain (ε_c). Creep then is allowed to proceed and crazing starts to take place when the strain reaches ε_c. For ethylene glycol and diethylene glycol, presumably due to their large differences from the solubility parameter (δ) of polystyrene (Table 1), crazing took 15 hours to complete. For 1-pentanol and triethylene glycol, only 4 1/2 minutes and 10 minutes were required respectively.

Figure 1 shows the loss tangent data for uncrazed polystyrene, and for those crazed in ethylene glycol and diethylene glycol respectively. The loss curves are nearly identical. To examine if any solvent loss has taken place during the transfer from the creep instrument to Rheovibron and during subsequent measurements, we compare in Figure 2 the loss curves of polystyrene crazed in triethylene glycol, and one simply immersed in the same solvent for the same length of time. Again the loss curves are very similar in shape, although the loss strength is higher for the crazed sample. The upswing of the loss curves are near the glass transition temperature of unplasticized polystyrene (105°C). Data in both Figures 1 and 2 indicate the essential lack of plasticization by the respective solvents.

The loss curves of polystyrene crazed and immersed in 1-pentanol are very different (Figure 3). Here the upswing in tan δ occurs around 60°C, which is near the glass transition temperature of the plasticized polystyrene (Table 1). The only plausible explanation for this exceptional behavior is that 1-pentanol has the lowest molecular weight and boiling point, hence the diffusion rate into the polymer should be the highest. As a consequence the uptake in the organic solvent into the polymer is sufficiently great to effect a lower T_g observable by dynamic mechanical measurement.

According to the plasticization mechanism of solvent crazing[4,5], the organic agent swells the polymer and act as a plasticizer in lowering the glass transition temperature. As a consequence, the resistance to flow should also decrease for the plasticized polymers, thereby alleviating the crazing stress. Our 1-pentanol data appear to be consistent with this mechanism. However, similar data for other solvents are more difficult to interpret. It is possible that plasticization took place on a surface layer of the polymer only and is insufficient to show up as a depression in the primary glass transition process. The very similar dynamic mechanical behavior of the immersed and crazed samples (Figures 2 and 3) indicates a uniform plasticization. If plasticization only occurred in the craze matter, then the polymer would have become a heterogeneous system and two glass transition processes should have been observed. However, it cannot ruled out that these organic liquids may have wetted the

the surfaces of the voids in the craze, thereby reducing the energy of craze formation[5,7]. Possibly for some liquids both the plasticization and surface energy mechanisms may be operative.

References

1. R. P. Kambour, Macromol. Rev., 7, 1 (1974).

2. J. T. Koberstein, S. L. Cooper and M. Shen, Rev. Sci. Instr. 46, 1639 (1975).

3. R. P. Kambour, C. L. Gruner and E. E. Romagosa, J. Polymer Sci. Phys. Ed., 11, 1879 (1973).

4. B. Maxwell and L. F. Rahm, Ind. Eng. Chem., 41, 1988 (1949).

5. G. A. Bernier and R. P. Kambour, Macromol., 1, 393 (1968).

6. H. A. Stuart, G. Markowski and D. Jeschke, Kunstoff, 54, 618 (1964).

7. R. L. Bergen, Jr., SPE J., 24, 77 (1968).

Acknowledgement

Figure Captions

Figure 1: Loss tangent versus temperature curves for uncrazed polystyrene, and for polystyrene crazed in ethylene glycol and diethylene glycol.

Figure 2: Loss tangent versus temperature curves for polystyrene crazed in triethylene glycol and immersed in the same solvent.

Figure 3: Loss tangent versus temperature curves for polystyrene crazed in 1-pentanol and immersed in the same solvent.

Table 1. Some Properties of the Polystyrene
and the Organic Liquids[*]

	Molecular Weight	b.p. (°C)	δ (cal/cc)$^{1/2}$	T_g[**] (°C)	ε_c (%)
Polystyrene	74,800	---	9.1	105	0.36
Triethylene glycol	150	290	10.7	---	0.27
1-Pentanol	88	138	11.1	63	0.21
Diethylene glycol	106	244	14.2	63	0.21
Ethylene glycol	102	197	17.1	102	0.36

[*] From Kambour, et. al.[3] Other data were taken from Lange's Handbook of Chemistry and Physics.

[**] Refer to the glass transition temperatures of pure polystyrene and plasticized polystyrene.

Polystyrene crazed in triethylene glycol for 10 min. (○)
Polystyrene immersed in triethylene glycol for 10 min. (●)

3.5 Hz